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**CLAIMS:**

1. A method of analyzing a stream of ions, the method comprising:
  - (1) subjecting a stream of ions to a first mass analysis step, to select ions having a mass-to-charge ratio in a first desired range;
  - (2) passing ions in the selected range into a radio frequency linear ion trap (Q2) containing a gas;
  - (3) trapping the selected ions in the linear ion trap (Q2) and exciting the ions to cause collisions with the gas and fragmentation;
  - (4) subjecting the fragmented ions to a secondary excitation, different from the first excitation, to cause excitation and fragmentation of selected fragment ions; and
  - (5) passing the ions out of the linear ion trap (Q2) and subjecting the ions to a further mass analysis step to determine the mass spectrum of the ions.
2. A method as claimed in Claim 1, which includes, prior to the additional step of secondary excitation, applying a signal to the linear ion trap (Q2), to isolate ions having a mass-to-charge ratio in a second desired range, wherein the secondary excitation step comprises exciting ions in the second desired range.
3. A method as claimed in Claim 2, which includes, while trapping the ions in the linear ion trap (Q2), effecting multiple cycles of:
  - (1) isolating ions having a mass-to-charge ratio in a further desired range; and
  - (2) exciting the isolated ions in the further desired range

to cause fragmentation.
4. A method as claimed in Claim 1, 2, or 3 wherein step (2) comprises passing the ions into the linear ion trap (Q2) with sufficient energy to promote collision induced dissociation, the said energy providing the

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excitation of step (3), whereby step (3) comprises applying a signal to the linear ion trap (Q2) to trap ions before subjecting the ions to the further mass analysis of step 4).

5 5. A method as claimed in Claim 1, 2, 3 or 4 which comprises exciting the ions in the linear ion trap (Q2) by providing an additional signal to the linear ion trap (Q2) to effect resonant radial excitation of ions.

10 6. A method as claimed in any preceding claim, wherein the further mass analysis step of step (5) is carried out in a quadrupole mass analyzer (Q3).

15 7. A method as claimed in any of claims 1 to 6, wherein the further mass analysis step of step (5) is carried out in a time of flight mass analyzer (40).

20 8. A method as claimed in Claim 7 wherein the further mass analysis step is carried out in a time of flight mass analyzer (40) arranged with its axis perpendicular to the axis of the linear ion trap (Q2).

25 9. A method as claimed in Claim 1 wherein each mass analysis step is carried out in one of: a linear quadrupole (Q3); a linear time of flight analyzer (40); a reflectron time of flight analyzer; a single magnetic sector analyzer; a double focusing two sector mass analyzer having an electric sector and a magnetic sector; a Paul trap; a Wien filter; a Mattauch-Herzog spectrograph; ion cyclotron mass spectrometer; and a Thomson parabolic mass spectrometer.

30 10. A method as claimed in Claim 6, 7, 8, or 9, wherein the first mass analysis step is carried out in a quadrupole mass analyzer (Q1) which is coaxial with the linear ion trap (Q2).

11. A method as claimed in Claim 1, which includes, prior to exciting the ions in step (3), subjecting the trapped ions to a signal comprising a

- plurality of excitation signals uniformly spaced in the frequency domain and having a notch, wherein the notch covers a desired frequency band and there are no excitation signals in the frequency band of the notch, and wherein the excitation signals have sufficient magnitude to excite and eject ions except for 5 ions having an excitation frequency within the frequency band of the notch.
12. A method as claimed in Claim 11, which comprises applying a combination of signals comprising sine waves and with frequencies up to  $f/2$ , where  $f$  is the frequency of the trapping RF.
- 10 13. A method as claimed in Claim 11, which comprises applying a combination of signals having sine waves with frequencies in the range 10 to 500 kHz and spaced at 500 Hz intervals, and the frequency band of the notch has a width of 1-10 kHz and is centered on the resonant frequency of an ion of 15 interest.
14. A method as claimed in Claim 11, 12 or 13 which includes, after selection of a desired ion, exciting the desired ion with a signal comprising a sine wave at or near the resonant frequency of the ion.
- 20 15. A method as claimed in Claim 7, which includes providing an exit lens (33) between the linear ion trap (Q2) and the time of flight device (40), and lowering the voltage on the exit lens (33) to permit ions to pass into the time of flight device (40), the method further comprising providing a signal to 25 a repeller grid (44) of the time of flight device (40), to cause the time of flight device (40) to scan at a desired rate.
16. A method as claimed in Claim 15, which comprises passing ions, in step (2), into the linear ion trap (Q2) for a period of substantially 5ms 30 subjecting the ions in the linear ion trap (Q2) to an excitation signal to excite and eject undesired ions for a period of substantially 4ms, exciting the desired ions for a period of substantially 4ms and passing the ions out of the linear ion trap (Q2) and scanning the time of flight device (40) for substantially 7ms.

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17. An apparatus (10), for effecting mass analysis and fragmentation of an ion stream, the apparatus comprising:  
an input (12) for an ion stream;  
a first mass analyzer (Q1);  
5 a radio frequency linear ion trap (Q2);  
a final mass analyzer (Q3); and,  
an auxiliary drive (84) connected to the radio frequency linear ion trap (Q2) for effecting multiple excitation steps.
- 10 18. An apparatus as claimed in Claim 17, wherein the first mass analyzer (Q1) comprises a quadrupole mass analyzer.
19. An apparatus as claimed in Claim 17 or 18, wherein the final mass analyzer (Q3) comprises a quadrupole mass analyzer, and the first mass analyzer (Q1), the linear ion trap (Q2) and the final mass analyzer (Q3) are axially aligned with one another.
20. An apparatus as claimed in Claim 17 or 18, wherein the final mass analyzer (Q3) comprises a time of flight device (40).
21. An apparatus as claimed in Claim 19 or 20, wherein the linear ion trap (Q2) includes a multipole rod set.
22. An apparatus as claimed in Claim 21, wherein the linear ion trap (Q2) comprises a quadrupole rod set and wherein the rods of the mass analyzers (Q1 and Q3) and of the linear ion trap (Q2) have substantially similar radii and substantially similar spacings.
23. An apparatus as claimed in Claim 17, wherein each of the first analyzer (Q1) and the final analyzer (Q3) comprise one of: a linear quadrupole; a linear time of flight analyzer (40); a reflectron time of flight analyzer; a single magnetic sector analyzer; a double focusing two sector mass analyzer having an electric sector and a magnetic sector; a Paul trap; a Wien filter; a Mattauch-Herzog spectrograph; an ion cyclotron mass spectrometer; and a Thomson

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parabolic mass spectrometer.

24. An apparatus as claimed in Claim 23, wherein the linear ion trap (Q2) includes a multipole rod set.

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25. An apparatus as claimed in Claim 17 or 22, wherein the linear ion trap (Q2) has a pair of opposed x rods and a pair of opposed y rods, wherein a main RF drive (86) is connected to the x and y rods (88 and 90) of the linear ion trap (Q2), and wherein the auxiliary drive (84) is connected to at least 10 one pair of rods of the linear ion trap (Q2).

26. An apparatus as claimed in Claim 25, wherein the auxiliary drive (84) is connected to the y rods (90) of the linear ion trap (Q2) through a transformer (85), and wherein the main RF drive (86) is connected directly to 15 the x rods (88) of the linear ion trap (Q2) and, through a coil of the transformer (85) to the y rods (90).

27. An apparatus as claimed in Claim 25, which includes an arbitrary waveform generator (82) connected to the auxiliary drive (84), for 20 applying a selected waveform to the linear ion trap (Q2) to excite ions therein.

AMENDED